the disordered Si(111) 1×1 surface. Then the observation of SiH_4, a stable species in the gas phase, on the (311) surface should be taken as evidence of the existence of the SiH_3 surface phase.

Another important observation is that the obtained energy distribution in the field evaporation of Si is wide, almost 35 eV (half-width at half-maximum), compared to an energy spread of less than 10 eV in the case of a metal in the dc evaporation mode.[17,20] This striking difference may be a result of the fact that field penetration at the semiconductor surface is very large compared to that at a metal surface where the screening length is an angstrom or so.[24] The energy distribution in field evaporation is of great interest and is the basic quantity for developing a good field-evaporation theory.

In conclusion, we have demonstrated the unique capability of a magnetic-sector atom-probe FIM to give important results in a semiconductor-surface study. Using Si emitters we have detected and identified silicon Si^+, silicon monohydride SiH^+, silicon dihydride SiH_2^+, and silane SiH_4^+ as field-evaporation products from various surface regions. These observations can be taken as evidence for the formation of silicon dihydride and trihydride surface phases upon their interaction with hydrogen as well as the monohydride surface phase.

We are grateful to R. H. Good, Jr., J. E. Rowe, H. D. Hagstrum, E. I. Givargizov, and T. T. Tsong for helpful discussions and comments on this study. This work was supported by the Research Initiation Grant of The Pennsylvania State University and by the National Science Foundation.

[a]Deceased.

[1]G. E. Becker and G. W. Gabeli, J. Chem. Phys. 38, 2942 (1963).
[2]H. Ibach and J. E. Rowe, Surf. Sci. 43, 481 (1974).
[3]J. A. Appelbaum and D. R. Hamann, Phys. Rev. Lett. 34, 806 (1975).
[4]T. Sakurai and H. D. Hagstrum, Phys. Rev. B 12, 5349 (1975).
[5]K. C. Pandey, T. Sakurai, and H. D. Hagstrum, Phys. Rev. Lett. 35, 1728 (1975).
[6]T. Sakurai and H. D. Hagstrum, J. Vac. Sci. Tech. 13, 807 (1976).
[7]T. Sakurai, M. J. Cardillo, and H. D. Hagstrum, J. Vac. Sci. Tech. 14, 397 (1976).
[8]T. Sakurai and H. D. Hagstrum, Phys. Rev. B 14, 1593 (1976).
[9]T. Sakurai and H. D. Hagstrum, to be published.
[10]J. A. Appelbaum, G. A. Baraff, D. R. Hamann, H. D. Hagstrum, and T. Sakurai, to be published.
[11]J. E. Rowe and H. Ibach, Phys. Rev. Lett. 32, 421 (1974).
[12]F. Jona, H. D. Shih, A. Ignaliev, D. W. Jepsen, and P. M. Marcus, to be published.
[13]M. B. Webb, Bull. Am. Phys. Soc. 21, 936 (1976).
[14]E. W. Müller, J. A. Panitz, and S. B. McLane, Rev. Sci. Instrum. 39, 83 (1968).
[15]A. J. Melmed and R. J. Stein, Surf. Sci. 49, 645 (1975).
[16]A. J. Melmed and J. A. Panitz, private communication.
[17]E. W. Müller and T. Sakurai, J. Vac. Sci. Tech. 11, 878 (1974).
[18]T. Sakurai, E. W. Müller, R. J. Culbertson, and T. T. Tsong, to be published.
[19]H. Ibach and J. E. Rowe, Phys. Rev. B 10, 710 (1974).
[20]A. R. Waugh and M. J. Southon, J. Phys. D 6, 1017 (1976).
[21]E. W. Müller, S. V. Krishnaswamy, and S. B. McLane, Phys. Rev. Lett. 31, 1282 (1973).
[22]T. Sakurai, T. T. Tsong, and E. W. Müller, Phys. Rev. 181, 530 (1969).
[23]D. C. Gupta, Solid State Tech. 14, 33 (1971).
[24]T. T. Tsong and E. W. Müller, Phys. Rev. 181, 530 (1969).

Cluster Mean-Field Theory of Spin-Glasses

C. M. Soukoulis and K. Levin
The Department of Physics and The James Franck Institute, The University of Chicago, Chicago, Illinois 60637
(Received 18 April 1977)

In view of the large amount of experimental evidence in support of a cluster description of the spin-glasses, we propose and solve a mean-field model of these systems in which dynamical clusters are the basic entity. The model can explain an important and unresolved puzzle: why the susceptibility has a cusp at a freezing temperature T_c, while the specific heat has a rounded maximum at a significantly higher temperature.

One of the most puzzling features of the spin-glasses (dilute alloys such as *Cu*Mn and *Au*Fe) is their "dual" nature: Measurements of the static low-field susceptibility χ,[1] Mössbauer splitting,[2] and muon-precession rate[3] suggest that these alloys exhibit a sharp phase transition at

a freezing temperature T_c. Thermoelectric power,[4] resistivity,[5] and magnetic specific-heat[6] C_m measurements do not reveal any anomalies at T_c. Moreover, C_m generally has a broad maximum at a temperature T_c about 20–40% above T_c. Theoretical approaches to a study of the spin-glasses have been equally divided and only partially successful. Mean-field theories[7,8] lead to sharp anomalies in *both* χ and C_m. Also inconsistent with experimental observations are the cluster theories[9,10] based on the notion of thermal blocking of rigid clusters of spins. While these can explain some hysteresis effects[9]—the magnitude of the zero-temperature resonant magnetization[10] and field-sensitivity experiments[10]—they predict[9] a rounded peak in χ. The cluster percolation theory of Smith[11] yields a cusp in χ, but the behavior of C_m near T_c is indeterminate.

The purpose of this Letter is to propose a simple model for the spin-glasses which incorporates both the mean-field–theoretic and cluster notions. In this way, it is shown how a sharp cusp in χ can appear at T_c, while at the same time the specific heat exhibits a broad maximum at a higher temperature. In contrast to previous *rigid*-cluster theories,[9-11] we emphasize here that the internal dynamics of the clusters are important and play an essential role in determining the behavior of C_m.

The cluster model Hamiltonian is given by

$$H = -\sum_{\nu<\lambda} J_{\nu\lambda}\vec{S}_\nu\cdot\vec{S}_\lambda - \sum_\nu\sum_{i<j} J_{ij}^{0}\vec{S}_{i\nu}\cdot\vec{S}_{j\nu}, \tag{1}$$

where J_{ij}^{0} is the intracluster exchange constant and $J_{\nu\lambda}$ the randomly distributed intercluster exchange constant. In order for the cluster concept to make sense, the former interactions are assumed stronger than the latter. Greek indices refer to a particular cluster and Roman indices to a given spin within that cluster. Here $\vec{S}_\nu = \sum_i \vec{S}_{i\nu}$ is the total spin of a cluster. Thus the first term in the Hamiltonian describes interactions between clusters while the second refers to intracluster interactions. We assume that $J_{\nu\lambda}$ is independent of the spin indices i and j. This is justified provided the clusters are sufficiently far apart so that the intercluster exchange interactions are insensitive to the location of the spins *within a cluster*. For simplicity we take the clusters to be identical in size and shape. These then represent the average cluster in the alloy. The effects of including a distribution of cluster sizes within mean-field theory (in which all but one cluster is averaged over) are quantitative rather than qualitative. These will be discussed below. The model may be justified from a phenomenological point of view. A rather complete list of experimental support for it is given in Ref. 10. Microscopically, one may view the clusters as units of spins which are spatially interconnected and therefore strongly correlated. While these will occur in any statistically random arrangement of impurities, chemical clustering, which is usually present, will enhance their effects.[12] As in the theory of Edwards and Anderson[7,8] (EA), the intercluster exchange interactions which are given by a near-neighbor Gaussian distribution,

$$P(J_{\nu\lambda}) = (2\pi)^{-1/2}J^{-1}\exp(-J_{\nu\lambda}^{2}/2J^{2}), \tag{2}$$

are treated within a random-mean-field theory. The intracluster interactions, however, are treat treated exactly.

The free energy is calculated with use of the replica method, which is believed to be reliable for temperatures at and above T_c. It is this temperature region which we will focus on here. We find that

$$F = -kT\lim_{n\to 0} n^{-1}\left[\int \Pi\, dJ_{\nu\lambda}\,\mathrm{Tr}_n \exp\Big(\beta\sum_\alpha\sum_{\nu<\lambda} J_{\nu\lambda}\vec{S}_\nu^{\alpha}\cdot\vec{S}_\lambda^{\alpha} - \beta\sum_\alpha\sum_\nu H_{\mathrm{cl}}^{\alpha\nu}\Big)\Pi P(J_{\nu\lambda}) - 1\right], \tag{3}$$

where the intracluster Hamiltonian is

$$H_{\mathrm{cl}} = -\sum_{i<j} J_{ij}^{0}\vec{S}_i\cdot\vec{S}_j \tag{4}$$

and where the trace is taken over n replicas labeled α of the actual system.

To evaluate the integral in (3), a mean-field approximation of the intercluster interaction is used so that commutators like[7] $[\vec{S}_\nu\cdot\vec{S}_\lambda, \vec{S}_{i\nu}\cdot\vec{S}_{j\nu}]$, etc., with $\nu\neq\lambda$, are set equal to zero. Our mean-field decoupling of the resultant expression for F introduces two variational parameters: $q = \langle\vec{S}_\nu^{\alpha}\cdot\vec{S}_\nu^{\beta}\rangle$ for $\alpha\neq\beta$, and $M = \langle\vec{S}_\nu^{\alpha}\cdot\vec{S}_\nu^{\alpha}\rangle$. The former is analogous to the usual EA spin-glass order parameter. It differs only in that S_ν denotes the cluster spin rather than the spin of one impurity atom. Here M is the total spin of each cluster; in the EA theory the analogous parameter is a (nonvariational) constant. Follow-

ing Refs. 7 and 8, we find that the free energy per cluster is

$$F(q,M) = -kT\{[\bar{J}^2/12(kT)^2](q^2-M^2) + (2\pi)^{-3/2}\int d^3r\, e^{-r^2/2} \ln \mathrm{Tr} \exp(-\beta H^{\mathrm{eff}})\}, \quad (5)$$

where

$$-H^{\mathrm{eff}} = \sum_{i<j} J_{ij}{}^0 \vec{S}_{iv}\cdot\vec{S}_{jv} + \bar{J}(q/3)^{1/2}\vec{r}\cdot\vec{S}_v + (\bar{J}^2/6kT)(M-q)\vec{S}_v\cdot\vec{S}_v . \quad (6)$$

Here $\bar{J} = z^{1/2}J$ with z the number of cluster near-neighbors of a given cluster. In deriving (5) we have used the fact that all three terms in the effective cluster Hamiltonian H^{eff} commute with one another. The physical interpretations of the various contributions to H^{eff} are as follows: The first term is the intracluster exchange; the second represents the interactions of the random anisotropy field with the spins in the cluster. This field arises because of intercluster interactions and its strength is given in terms of the order parameter q. The third term is an effective ferromagnetic intracluster exchange term which also derived from intercluster interactions. In the usual mean-field theories, this is a c-number and is combined with the first term in Eq. (5).

The order parameters q and the cluster moment M are derived variationally by using $[\partial F(q,M)/\partial q]_M = 0$ and $[\partial F(q,M)/\partial M]_q = 0$. This yields the coupled equations, with $Z \equiv \mathrm{Tr}\exp(-\beta H^{\mathrm{eff}})$:

$$M = (2\pi)^{-3/2}\int d^3r\, e^{-r^2/2}\,\mathrm{Tr}(\vec{S}_v\cdot\vec{S}_v e^{-\beta H^{\mathrm{eff}}})/Z \quad (7)$$

and

$$M - q = (2\pi)^{-3/2}\int d^3r\, r\, e^{-r^2/2}(3/q)^{1/2}(kT/\bar{J})\,\mathrm{Tr}(\vec{r}\cdot\vec{S}_v e^{-\beta H^{\mathrm{eff}}})/Z . \quad (8)$$

When a distribution of cluster sizes is included we find that these equations are easily modified.[13] Because our numerical results (see below) show the same qualitative behavior for all cluster sizes we will consider, for simplicity, the distribution to be sharply peaked about some value N. Both the static susceptibility χ and the specific heat C_m per cluster may be calculated in terms of M and q,

$$\chi = g^2\mu_B{}^2(M-q)/3kT, \quad (9)$$

where $g\mu_B$ is the magnetic moment of an impurity atom. The specific heat is given by a sum of two terms, i.e.,

$$C_m = C_m{}^{\mathrm{inter}} + C_m{}^{\mathrm{intra}} . \quad (10)$$

The first contribution arises primarily from intercluster contributions and is equal to

$$C_m{}^{\mathrm{inter}} = \frac{d}{dT}[(\bar{J}^2/6kT)(q^2-M^2)], \quad (11)$$

while the intracluster contribution is

$$C_m{}^{\mathrm{intra}} = +\frac{d}{dT}\int d^3r\, e^{-r^2/2}\frac{\mathrm{Tr}(H_{\mathrm{cl}}\, e^{-\beta H^{\mathrm{eff}}})}{Z} . \quad (12)$$

Because it reflects the dynamics of a finite number of spins, $C_m{}^{\mathrm{intra}}$ has a rounded maximum as a function of temperature which occurs at the characteristic intracluster exchange-interaction energy. On the other hand, the first expression on the right-hand side of Eq. (10) yields a cusp-like contribution to C_m like that found by EA.

The magnitude of $C_m{}^{\mathrm{intra}}$ grows as the number of spins N in the cluster increases,[14] whereas for large N the magnitude of $C_m{}^{\mathrm{inter}}$ is independent of N.[7,8] It is because there are two distinct energy scales in the model, corresponding to the strength of the intracluster and intercluster exchange interactions, that the intracluster maximum occurs at a temperature T_0 which is different from—in fact higher than—T_c. At low T, the intracluster contribution varies as $e^{-1/T}$ while $C_m{}^{\mathrm{inter}}$ is linear in T as found experimentally.[6]

For clusters in which M is not strongly temperature dependent, we find from Eq. (9) that, as in previous mean-field theories,[7,8] the susceptibility χ has a sharp cusp at T_c. In this case, the characteristic interaction which determines the behavior of χ is the intercluster exchange.

We have performed numerical calculations to study systematically the results of our model for a wide range of parameters. We considered clusters containing $N \leq 6$ spins coupled by either near-neighbor ferromagnetic or antiferromagnetic exchange interactions. Because the intracluster contribution to the specific heat is smaller for the ferromagnetic than for the antiferromagnetic case,[14] the most favorable results and those which are illustrated here are for antiferromagnetic coupling. We also chose two values of the parameter N. For the case $N=3$ the ratio of the exchange constatns $|\bar{J}/J_0| = 0.55$, and for $N=6$ this was given by $=0.32$. While the parameters were chosen to yield reasonably good agreement with

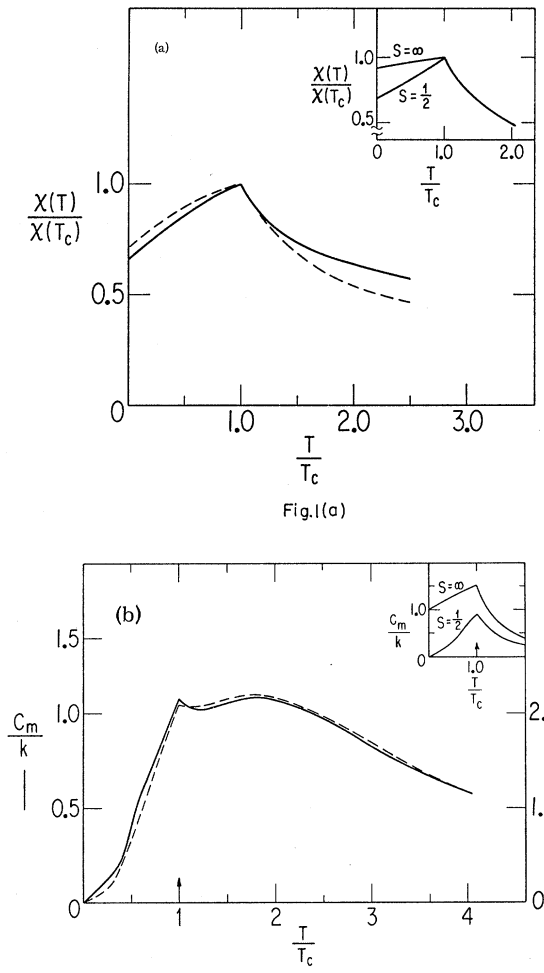

FIG. 1. Temperature dependences of the (a) static susceptibility and (b) specific heat per cluster for antiferromagnetic intracluster exchange interactions with $N = 3$ (solid curve) and $N = 6$ (dashed curve). In the insets are plotted the results obtained within the usual mean-field theory.

experiment, the results obtained were not atypical.

In Fig. 1(a) is shown the temperature dependence of the normalized susceptibility $\chi(T)/\chi(T_c)$. The solid (dashed) curve is for $N=3$ ($N=6$). The behavior of χ is similar to what is found in the quantum-mechanical generalization of the EA theory,[7,8] which is plotted in the inset. Because of the T dependence of M, we find that χ deviates slightly from a Curie-law behavior above T_c.

Finally, in Fig. 1(b) is shown the temperature dependence of C_m. The solid and dashed curves correspond to $N=3$ and $N=6$, respectively. A broad rounded maximum occurs at a temperature $T_0 \sim 1.7T_c$. There is also a small cusp at T_c. Fluctuation effects[15] may make this small feature undetectable experimentally. For comparison purposes, the quantum-mechanical EA-model results are plotted in the inset. It is evident that the model represents an improvement over this previous one which has a sharp cusp at T_c and decreases monotonically above this temperature in disagreement with experiment.

This work was supported by the National Science Foundation and by the National Science Foundation–Materials Research Laboratory. One of us (K.L.) acknowledges a fellowship from the Alfred P. Sloan Foundation.

[1]V. Cannella and J. A. Mydosh, Phys. Rev. B 6, 4220 (1972).

[2]B. Window, in *Magnetism and Magnetic Materials—1974*, AIP Conference Proceedings No. 24, edited by C. D. Graham, Jr., G. H. Lander, and J. J. Rhyne (American Institute of Physics, New York, 1975), Vol. 1, p. 167.

[3]D. E. Murnick, A. T. Fiory, and W. J. Kossler, Phys. Rev. Lett. 36, 100 (1976).

[4]P. J. Ford *et al.*, Solid State Commun. 13, 857 (1973).

[5]P. J. Ford and J. A. Mydosh, Phys. Rev. B 14, 2057 (1976); and J. A. Mydosh *et al.*, Phys. Rev. B 10, 2845 (1974).

[6]L. E. Wenger and P. H. Keesom, Phys. Rev. B 11, 3497 (1975), and 13, 4053 (1976).

[7]S. F. Edwards and P. W. Anderson, J. Phys. F 5, 965 (1975); K. H. Fischer, Phys. Rev. Lett. 34, 1438 (1975).

[8]D. Sherrington and B. W. Southern, J. Phys. F 5, L49 (1975).

[9]J. L. Tholence and R. Tournier, J. Phys. (Paris), Colloq. 35, C4-229 (1974).

[10]K. Binder, Z. Phys. B 26, 339 (1977); see also K. Binder and K. Schroeder, Phys. Rev. B 14, 2142 (1976).

[11]D. A. Smith, J. Phys. F 4, L226 (1974), and 5, 2148 (1975).

[12]In a "correlated"-cluster (Ref. 10) rather than spatial-cluster description, the average cluster sizes should be taken to be T dependent. We have considered these effects and find that in the region of temperatures of interest (near T_c and above) our results are not qualitatively affected.

[13]The essential modification is to introduce a sum over the cluster size N times the probability distribution $P(N)$ on the right-hand side of these equations. That they are so little affected comes about physically because in mean-field theory a distribution in the size of averaged-over spins is not of particular significance.

[14]J. C. Bonner and M. E. Fisher, Phys. Rev. 135, A640 (1964).

[15]A. B. Harris, T. C. Lubensky, and J.-H. Chen, Phys. Rev. Lett. 36, 415 (1976); C. Jayaprakash, J. Chalupa, and M. Wortis, Phys. Rev. B 15, 1495 (1977).